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THE LOW-TEMPERATURE TRANSITION IN MAGNETITE

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Abstract: Magnetite has been shown to transform from the cubic to the orthorhombic system at temperatures below 119°K. The coefficients of thermal expansion above and below the transition are given.

Introduction

In a recent communication, Tombs and Rooksby[1] reported the transition of magnetite, Fe_3O_4, at 119°K to be from the cubic to the rhombohedral system. This observation was based on a careful study of the X-ray diffraction pattern below the transition, using photographic methods. Measurements made in this laboratory[2] on the magnetic anisotropy and conductivity of magnetite at temperatures below 119°K, strongly support the view proposed by Verwey et al.[3] that the transition is to the orthorhombic system. Further weight is lent to this proposal by recent strain-gauge measurements on single crystals of magnetite.[4]

A redetermination of the X-ray data, recorded with the Norelco Geiger-counter spectrometer, confirmed the low temperature form of magnetite as orthorhombic, and the pattern has been successfully indexed assuming the space group to be I_{mma}. The thermal expansion coefficient of the c axis be-

1) N. C. Tombs and H. P. Rooksby, Acta Cryst. 4, 474 (1951).

2) B. A. Calhoun, to be published.

3) E. J. Verwey, P. W. Haayman, and F. C. Romeijn, J. Chem. Phys. 15, 181 (1947).

4) L. R. Bickford, Jr. Paper presented at Office of Naval Research Conference on Magnetism, Washington, D. C., Sept., 1952. Abstract, Rev. Mod. Physics, in press.

comes negative below 119°K, and at about 95°K there is no appreciable difference in the spacings of (440) and (008). This appears to be the reason which led Tombs and Rooksby to the assignment of a rhombohedral system.

Experimental

A simple adaptation[5] of the Norelco Geiger-counter spectrometer has been devised for use at low temperatures, with the sample in thermal contact with a bath of liquid nitrogen. The temperature of the specimen is measured to within 2°K by means of a thermocouple in close contact with the sample holder. FeK_α radiation was used throughout (λ = 1.93597Å). The profiles of the X-ray diffraction lines were obtained by multiple counts of the intensities at intervals of not less than 0.05° 2θ across the reflection. At background level, about 1000 counts were recorded at each angle. Using the relation $P_f = 0.67/N^{1/2}$, the probable error in the intensity is 2.1 percent, which decreases at angles near the peaks.

The magnetite sample was prepared by reducing very pure, 325-mesh Fe_2O_3 in an atmosphere of 3.2 volume percent CO in CO_2 at 1000°C. The sample was kept at this temperature for 6 hours and annealed by cooling at a rate of 100°C per hour, increasing the CO content as described by Smiltens.[6] No sintering was observed in the product, the entire sample being passable through a 325-mesh screen. The X-ray powder pattern of this magnetite showed no trace of Fe_2O_3 or FeO, and the widths of the peaks at one-half height was less than 0.15° 2θ at all angles, thus indicating little or no residual strain.

Crystal Data

The unit cell side of cubic magnetite at 295°K was measured as 8.3940 ± 0.0005Å, in exact agreement with Tombs and Rooksby.[1] On cooling through

5) B. A. Calhoun and S. C. Abrahams, Tech. Report 62.

6) J. Smiltens, J. Chem. Phys. 20, 990 (1952).

the transition to 78°K, the cubic lines (800), (731) and (533), which are the three strongest high angle reflections ($2\theta_{hk\ell} > 90^{\circ}$) obtained with FeK_{α} radiation, each split into several lines. The best fit for these observed spacings and intensities corresponds to the orthorhombic unit cell a = 5.912, b = 5.945, c = 8.388 ± 0.005Å with space group $I_{mma} - D_{2h}^{28}$. This space group was arrived at by a consideration of the resulting symmetry if the electrons order in the manner proposed by Verwey et al.[3] The a and b axes are one half the face diagonals of the cubic modification. Increased accuracy could probably be obtained at liquid helium temperatures, which would require little modification of this technique. The observed and calculated spacings and intensities based on this cell are collected in Table 1. The intensities were calculated assuming the same atomic positions as in the cubic form, making due allowance for the transformation to the orthorhombic unit cell, and keeping an oxygen parameter of 0.375, since this atom contributes very little to the planes concerned.

Table 1. Intensities and spacings in orthorhombic magnetite.

hkℓ	d_{obs}	d_{calc}	I_{obs}	I_{calc} †
143	1.2804	1.2812	weak	65
035	*	1.2804	*	
305	1.2765	1.2774	medium	97 †
413	*	1.2762	*	
053	*	1.0942	very faint	20
251	1.0938	1.0937	faint	40
145	*	1.0933	*	40
343	1.0919	1.0923	faint	90 †
127		1.0922		
217	*	1.0916	*	59 †
433	1.0909	1.0909	faint	59 †
415	1.0901	1.0902	weak	80 †
521	1.0897	1.0894	medium	100 †
503	*	1.0890	*	
008	1.0481	1.0485	weak	50
440	1.0476	1.0481	medium	100

*Resolution was insufficient to permit location of these lines.

† Calculated intensities were normalized on the basis I(440) = 100.

† This intensity includes an α_2 component, assuming $I\alpha_1 = 2\ I\alpha_2$.

Thermal Expansion

The dimensions of the magnetite unit cell were measured at 295°, 128° and 78°K. The resulting volumes, 591.4, 589.1 and 589.6 $\mathring{A}^3$, respectively, referred to the cubic cell, are in excellent agreement with those given by Tombs and Rooksby.[1] From these data, and a determination of the c-axis length at 108°K, the coefficients of thermal expansion above and below the transition may be computed. These values are compared in Table 2 with those reported by others.

Table 2. Thermal expansion coefficients for magnetite.

Temp. (°K)	Method	Direction	Coefficient x 10^{-6}	Observer
295-128	X-ray	any	7.7	Present authors
295-165	X-ray	any	3.5	Tombs and Rooksby[1]
323-290	interferometric	any	8.6	Sharma[7]
173-123	dilatometric	any*	7.7	Domenicali[8]
108-78	X-ray	[001]	-20	Present authors
106-93	dilatometric	[001]	-10	Domenicali[8]

*Domenicali quoted different values for the [100], [110] and [111] directions: 7.7×10^{-6} is the average of these.

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7) S.S.Sharma, Proc. Ind. Acad. Sci. 31A, 261 (1950).

8) C.A.Domenicali, Phys. Rev. 78, 458 (1950).